EXPANDED TECHNICAL ASSISTANCE PROGRAM

FAO

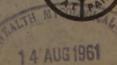
No. 1204

Report to the Government of TURKEY

PROTECTION, CHEMICALS
AND EQUIPMENT

RAME I

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
ROME, 1960





REPORT TO THE

GOVERNMENT OF TURKEY

ON

THE INSTITUTE FOR PLANT PROTECTION CHEMICALS AND EQUIPMENT,

ANKARA

by

H.S. Hopf FAO Expert on Insecticides

Rome, 1959



CONTENTS

	Page
INTRODUCTION	. 1
THE PROBLEM	2
Pesticide Consumption in Turkey	
The Residue Problem	
Present Facilities at the Institute	
SUMMARY OF ACCOMPLISHMENTS	. 12
Determination of Physical Characteristics of Formulations.	. 12
Determination of Chemical Properties of Formulations	. 13
Chemical Residue Analysis	. 13
Biological Residue Analysis	. 15
Future Work	. 15
CONCLUSIONS AND RECOMMENDATIONS	. 17
General Assessment and Further Training	. 17
Equipment	. 18
Organization	. 18
Cooperation with Other Government Bodies	. 19

INTRODUCTION

The Institute for Plant Protection Chemicals and Equipment (Zirai Mücadele Ilaç ve Aletleri Enstitüsü) in Ankara was founded by the Ministry of Agriculture in order to exercise control over the composition of pesticides and the quality of application machinery used for agricultural purposes in Turkey. It started functioning in January 1958 in temporary premises. Its tasks include the determination of the chemical and physical characteristics of pesticide formulations and the assay of pesticide residues in crops. Both chemical and biological assay methods are used. The Institute is also charged with testing the performance of spraying and dusting apparatus and with the search for suitable minerals to be used as diluents for pesticides formulated in Turkey.

In order to assist the Institute to organize and carry out a satisfactory program, the Food and Agriculture Organization of the United Nations appointed Dr. A.B. Hadaway as Expert on Pesticides, under the Expanded Technical Assistance Program. Dr. Hadaway served in Turkey from July to December 1958 and, among other achievements, he initiated the bio-assay project. His work was detailed in FAO Report No. 1041 entitled: "Report to the Government of Turkey on Pesticides".

In accordance with a request by the Government of Turkey for further technical assistance on the work of the Institute, FAO appointed Dr. H.S. Hopf to continue the work of Dr. Hadaway, with special stress on the assay of pesticides by chemical methods, particularly as residues on crops.

Dr. Hopf served as FAO Expert on Pesticides in Turkey from 17 June to 15 November 1959. Most of his time was spent in the training of staff in methods suitable for the detection and assay of small quantities of pesticides of the kind most frequently used in Turkey. He also advised on the facilities urgently needed for the proper functioning of the laboratories, and helped with certain aspects of the bio-assay work, including the breeding of test insects. A visit was paid to Istanbul in order to see some of the formulation plants of commercial companies and to discuss their future plans.

The expert's special thanks are due particularly to Mr. Necdet Kücükkoca, Acting Director of the Institute, without whose untiring help and advice no progress could have been made, and to Mrs. Jülide Kaya, Mrs. Cânâ Otaci and Dr. Ayten Güvener, of the Chemical Section of the Institute, who were most closely connected with him in his day-to-day duties. Their enthusiasm and diligence made cooperation with them a very great pleasure. Grateful acknowledgement is also made to the friendliness, kindness and cooperation of all the other technical staff, in particular to Mr. Talip Öden of the Bio-assay Section, Mr. Hüseyin Ayhangel of the Physical Chemistry Section and Mr. Kazim Ulaşan of the Machinery Section. Finally, the expert wishes to thank Mr. Nahit Teoman, Section Director in the Office of the Director-General of Plant Protection and Plant Quarantine, who supplied the material for the tables on pesticide consumption incorporated in this report.

THE PROBLEM

Pesticide Consumption in Turkey

The function of the Institute within the agricultural economy of Turkey can perhaps be best understood against the background of pesticide consumption. Figures on actual use, - in tons applied or hectares treated, - are not available, but there are data on imports of formulated products, and of active ingredients imported for formulation by Turkish industry.

Apart from copper sulphate and sulphur dust, all active ingredients of significant use are imported. All such imports for agricultural purposes are channeled through the Agricultural Supply Organization (Zirai Donatim Kurumu) and a fairly complete picture should be presented in the following tables of all purchases by the Ministry for direct use, and of purchases of imported formulations by the growers. The consumption of pesticides formulated in Turkey for sale to growers is more difficult to ascertain. Tables 1 through 5 show purchases of pesticides and application equipment for the first three quarters of 1959. The figures are partly based on estimates.

Imports for the remainder of 1959 are expected to cost \$450,000 for active ingredients to be used mainly for the production of 3,500 tons of insecticidal dust, and \$750,000 for formulated material, mostly based on phosphoric esters. Of the latter, the Ministry is expected to buy \$330,000 worth, and the rest is to be sold on the open market.

There are no figures for the amounts of pesticides formulated in Turkey for sale to growers and contractors. It would be misleading to deduce them from the ingredients imported after deduction of Government consumption. 1958 was a year of acute currency shortage in which imports were drastically reduced, and it is likely that some of the material imported in 1959 is being carried over for use in 1960. One would, however, hazard a guess that grower consumption of such formulations was in the order of Government consumption. It would consist entirely of insecticides, mostly in the form of dusts. In addition to pesticides with imported ingredients, Donatim sold 125 tons of copper sulphate and 4,000 tons of sulphur dust of Turkish origin to growers.

Some figures for previous years are given in FAO Report No. 1041. They are, however, not comparable to those here presented as they were arrived at in a different way, and recording by the Ministry and Donatim in the last few months was on a more extensive basis. Nor would such a comparison show very much, as consumption was, and still is, largely governed by consideration of the foreign exchange situation rather than demand.

Nevertheless, it is clear that, taking the last few years as a whole, there has been a rapid increase in pesticide consumption. There is every reason to think that this tendency will continue. A major national effort is being made to increase agricultural output, and it is agreed that plant

Table 1. Pesticides imported as formulations for purchase by the Ministry of Agriculture during the first three quarters of 1959.

Description	. Use	Amount (tons or 1000 1.)	F.o.b. price (\$ 1000)*	Price to Ministry (TL 1000)**
Insecticides:			200 P. J.	
50% DDT wettable powder 3% Isochlorthion dust 5% Dipterex dust 50% Dipterex cm.conc. Folidol E 605 em.conc. (35% a.i.)	Fruit pests Aelia(wheat) Sunn pest Olive pests ditto	462 241 139 33	198 94 50 100	3250 1984 1065 1543 1367
Ovicide Universal DNC winter wash	Fruit pests ditto	55 356	9 52	139 1107
Fumigants:				
Methyl bromide Ethylene dibromide	Cotton Soil insects	21 1	27	477 9
Fungicides:				
Flotox micronize (wettable sulphur)	Fruit, etc.	100	19	341
Perenox (copper)	ditto	22	10	141
Seed dressings:				
Leytosan (Hg)	Wheat diseases	700	174	2583
Cerosan (Hg) Combined Hg + HCB	ditto ditto	453) 50)	175	2924
Amatin (10% HCB)	ditto	300	44	?
Selective weedkillers:				
Hedonal flüssig U 46 special Cebetox	? ?	131 10 35	84 11 16	1236 190 231
Rodenticides: Strychnin sulphate	Rats, etc.	3	75	1345

Total

1238.5 19933***

* Price paid by the Agricultural Supply Organization.

** Final price paid by the Ministry of Agriculture to the Agricultural

Supply Organization.

^{***} At an exchange rate of \$1:TL9, the price to the Ministry contained an average foreign currency content of 56 per cent, or, conversely, the f.o.b. price was 56 per cent of the final price converted into TL.

Table 2. Pesticides imported as formulations for purchase by growers, etc., during the first three quarters of 1959.

Description	Amount(tons	F.o.b. price
	or 1000 1.)	(\$ 1000)
Insecticides:		1,1%
DNC winter washes	192	29
White oil formulations	294	54
3:10:40 dusts (BHC:DDT:S)	344	125
Aldrin 40% wett.powd.	63	67
Endrin 19.5% em.conc.	157	280
Parathion em.conc. (mostly 20% a.i.)	48	246
Ovicide	25	4
Fumigants:		
DD mixture	?	. 4
Fostoxin	25	171
Methyl bromide	7	9
Chlorosol	6	38
Fungicides:		
Copper formulations	202	83
Copper sulphate	2642	728
Wettable sulphur	. 82	22
Weedkillers:		1
Atlacide	148	45
Selective weedkillers(various)	100 - 110	129
Rodenticides:		
Various	103	2098

^{*} The price to the consumer cannot be ascertained, and is presumed to vary considerably according to district, type of package and quantity.

Table 3. Active ingredients imported for formulation in Turkey during the first three quarters of 1959.

Description "	Amount (tons)	F.o.b. price (\$ 1000)	F.o.b. price per ton
Technical DDT Technical BHC (15% gamma isomer) Technical BHC (50% gamma isomer) Lindane	1549 1093 287	769 202 257 70	496 185 (1230 per ton gamma)* 897 (1794 per ton gamma)* 2940
Technical Endrin 90% Toxaphene Technical Heptachlor Technical Diazinon Technical Tedion	14 130 38 29 75kg•	102 74 58(?) 167	728 567 1525(?) 5760

Total

.1699

Table 4. Pesticides formulated in Turkey for purchase by the Ministry of Agriculture during the first three quarters of 1959.

Description	Use	Amount (tons)	Dollar content (\$ 1000)*	Price to Ministry (TL 1000)
2.6% gamma BHC bait 2:10:0 BHC:DDT dust 3:10:0 BHC:DDT dust	Locust <u>Aelia</u> Sunn pest	: 364 2250 2505	12 173 225	415 6557 7347
10% DDT dust 2.5% Heptachlor dust 50% Toxaphene em.conc. 25% DDT em.conc.	Scythris Sunn Pest Nut weevil Fruit pests Various	3850 400 200	192 15 62 7	6213 822 4000 337
Basudin EMT em.conc. (20% Diazinon+5% DDT) Basudin EM em.conc. (20% Diazinon) DNC Universal winter wash	Olive fly ditto Fruit pests	15 80 400	18 92 ?	525 2400 1280
Total	11010 20000	400	796	29896**

Total

<u>96</u> <u>29896**</u>

In addition the Ministry bought 70 tens of sulphur dust produced from Turkish raw materials.

^{*} Average price per ton gamma isomer as crude BHC: \$1343.

^{*} Estimated from the data in Table 3.

^{**} At an exchange rate of \$1:TL 9, the price of the above (excluding DNC winter wash) contained an estimated foreign currency content of 25 per cent or, conversely, the dollar content paid by the Agricultural Supply Organization was 25 per cent of the final price converted into TL.

Table 5. Plant protection machinery and spares imported during the first three quarters of 1959.

- Description	Numbers	F.o.b. price (\$ 1000)
Motor dusters, various	1084	209
H.V. sprayers, various	279	126
Swing fog apparatus	?	10
Electrical warehouse sprayers	14	1
Dual purpose motor knapsacks	100	24
Aircraft	2	18
Total	and the state of t	388

protection has an important role to play. All the existing formulation factories are planning on this basis, and others are going ahead with plans for the erection of new plant, mostly in association with industry abroad. It is one of the major duties of the Institute to ensure that all materials reaching the market conform to the specifications laid down by the Government.

For purchases by the Ministry this is already fully implemented. Every batch of formulation produced in Turkey is sampled for analysis. Products not reaching the required standard are rigorously rejected. Formulations produced abroad are submitted for registration and are then equally subjected to analysis, as are all "complaint" samples which are sent to the supplier by the consumer when the latter thinks that the pesticidal properties do not measure up to specifications or expected performance.

An approval scheme for formulations to be sold on the open market for agricultural purposes is about to be started. Under it all products meeting Government specifications will bear a special label. The Institute is the Government's chief agent for establishing the requirements in cooperation with the Plant Protection Institutes, and for determining whether marketed products meet them. It may be said at this point that information on which to base these specifications is not sufficiently available for Turkish conditions, and data obtained from abroad, which may not be strictly applicable to the use proposed for the material in Turkey, are too often all the guidance extant. It is to be hoped that the six Plant Protection Institutes, which are the chief organs for testing under practical conditions, will give much more help in this work.

The tables show that the price of formulations produced in Turkey has a foreign currency content of 25 per cent, as opposed to one of 56 per cent for imported finished products. With an adverse balance of trade, it is

clearly of the utmost interest to Turkey to possess an efficient formulation industry, capable of supplying an increasing demand with quantity and quality products. The help the Institute can give in this respect, to both producer and consumer, can hardly be overrated.

It has been the experience of many countries that the rapid rise in the consumption of plant protection chemicals, which has taken place in recent years, has shown itself first in the insecticide field, with the development of fungicides and weedkillers following. Turkey seems to be in the early stages of such an evolution. It is shown in the tables that insecticides have much the largest share of the market. Fungicide consumption is low and seems to be confined to copper, sulphur and seed dressings, and selective weedkillers have been imported in significant quantities for the first time in 1959. Though some parts of the country are so dry that the incidence of fungal disease is low, it may be confidently predicted that fungicides and, particularly, weedkillers will be used more and more widely, and will increase in proportion of total chemicals used as well as in absolute figures.

Compared with most other countries. Turkey is still using a very high proportion of her pesticides in the form of dusts. This is partly due to difficulties of water supply in many regions, but may also be attributed to problems of production and application. So far the native industry has been unable to produce a wettable powder meeting Government specifications (though it is hoped to manufacture limited quantities of wettable sulphur, BHC and DDT wettable powders in 1960). Emulsions are being made, but capacity is limited, and quality has not always been uniformly good. Low-volume spraying equipment, which makes best use of these types of formulations, is not available in sufficient quantities. When these difficulties are overcome. - as they are bound to be within the next few years, - there is no reason to assume that Turkey will not follow the usual pattern, and that emulsions and wettable powders will gain ground at the expense of dusts. The Institute has a vital part to play in this evolution, both by control of quality and by actively helping in the search for native ingredients.

Suitable fillers from native minerals for wettable powders are still urgently needed. The Institute hopes to devote some effort to this problem and to that of improved dust formulations. So far, it lacks experience and equipment for this work. A visit abroad by a member of the staff to study the relevant methods would be of great benefit to the Institute and therefore to the Turkish economy.

Turkey possesses very varied climatic and agricultural conditions, and each region has its own problems of plant protection. Six plant protection institutes are trying to solve these problems. The tables show the major posts controlled by direct action by the Ministry of Agriculture. Forestry has received little or no attention so far, but there is no doubt that the present drive for the rohabilitation of degraded forests and the planting of now ones will pose problems before long. Among crops protected by the growers themselves, cettin, tobacco and grapes may be mentioned, - all vitil components of the country's export

trade. There is, potentially at least, a demand for a much wider range of chemicals than is available at present. Systemics, for instance, are now not used at all. When every pest is being fought by the best means available, one should expect that there will hardly be a type of pesticide not used in Turkey. A considerable increase in the variety as well as the quantity of chemicals examined by the Institute must therefore be anticipated, and this is already reflected by the large number of samples received from abroad for testing and registration.

The Residue Problem

The present situation in Turkey with regard to safeguarding operator, consumer and wildlife from the consequence of improper use of pesticides must be described as disquieting. Legislation enabling the Ministry of Agriculture to make regulations exists and appears to be satisfactory, but in the absence of the necessary data and assay facilities these regulations cannot be issued, - nor could they be enforced. For safety precautions during application itself, e.g., gas masks and protective clothing, experience from abroad can probably be applied to Turkish conditions but, on such questions as the safe interval between application and harvest and the tolerance level of residues the necessary information on which to base the regulations can, in most cases, only be obtained by the estimation of pesticide residues under prevailing conditions.

The authorities are acutely aware of the importance of this problem. Cases of poisoning occur every year. Some of them may not even come to their notice as they are not always recognized in all parts of the country. In addition to such cases, Turkey has a peculiar problem in the Porphyria disease, endemic in the Diyarbakir Province, which has focussed wide-spread attention on the residue problem. This disease (or diseases), called locally 'Kara-Yara' (black blister) and 'Pombe Yara' (pink blister), occurs in certain townships of the province and is characterized by ulceration of the parts of the body exposed to the sun, abnormal pigmentation and loss of weight. There have been well over a thousand cases in the last few years, many of them fatal, particularly among children, including breast-fed babies. It has been attributed to the consumption of bread made with wheat seed dressed with fungicides, specially hexachlorobenzene. This assumption is, however, not universally accepted.

It is of the greatest importance to be able to determine the presence of seed dressings, HCB or mercurial, on grain or in grain products. The Institute is now in a position to do so, but until very recently the Ministry of Agriculture had no laboratory at its disposal capable of carrying out such an analysis.

The incidence of Porphyria furthermore highlights the need for facilities for investigations into the toxicological aspects of pesticides. No such facilities exist at present within the Ministry's organization, and it must needs rely on data from abroad. If HCB is indeed the causative agent of the disease, this effect will have been observed for the first time as no similar cases have been reported.

As a further example for the necessity for reliable residue estimation, the control of olive fly may be quoted. This insect is as serious a menace in Turkey as it is in comparable Mediterranean countries, and phosphoric esters are increasingly used for the protection of the crop. At present no analysis of olives or clive oil is carried out to establish the data on which safe intervals between treatment and harvest, combined with maximum efficiency of control operations, can be based.

Other important agricultural and horticultural uses of pesticides where residue problems are likely to arise include parathion on tobacco, DDT and BHC on alfalfa and other fodder plants, and a whole range of insecticides on all kinds of vegetables and fruits. The last-named are particularly important in view of the plans to establish the country as a major exporter of fresh fruit.

Apart from the safety factor, residue analysis often presents the most reliable way of assessing the efficacy of application machinery and other aspects of the methods of treatment.

There is at present only one laboratory in Turkey in which estimations of posticide residues can be carried out, namely the Institute, and even there work is only at the very beginning. Before the expert's arrival, certain bio-assay estimations were carried out, and the skills necessary for some chemical and biochemical determinations have now been acquired. It must, however, be stressed that because of lack of space and equipment, and the pressure of other problems, no large-scale contribution can be expected until the Institute is rehoused in accommodation suitable for such work, and its tasks have been replanned accordingly. Given the proper facilities, and given further a continuation in the training of staff (as is already being provided for), the Institute should be capable of giving a good residue assay service to the country, though it will take time for this service to reach maximum efficiency.

The Institute's task in this field will not end with the carrying out of estimations. It is highly probable that the plant protection institutes, which carry out field tests on all pesticides in their own region, will sooner or later feel the need for assessing fully the results of their own experiments. All over the world, such results nowadays include data on chemical residues as well as on central of the pest. It will be necessary for the Institute to help these stations in acquiring the necessary skill and equipment.

The setting-up of toxicological services is at present under consideration by the Ministry. If it is intended that a new unit be set up and form part of the Institute, help and advice from abroad will certainly be needed. However, practical work on this problem can not be started in the present premises.

Present Facilities at the Institute

To cope with the many problems utlined in the previous pages, the technical staff of the Institute is divided into four laboratories:

- (1) Chemical laboratory. This deals with all chemical analysis of formulations and residues.
- (2) Physical chemistry laboratory. This assesses the physical properties of formulations, e.g., suspensibility of wettable powders, emulsion stability, particle size, dustability and flowability. It is also charged with the search for new minerals for incorporation is inerts into home-produced formulations.
- (3) Bic-assay laboratory. This is responsible for all bio-assay work, including the breeding of test insects.
- (4) Machinery laboratory. This unit tests all dusting and spraying equipment proposed for use in Turkey.

There is also a small but well-chosen library, and the Institute has just published the first issue of "Bitki Koruma Bülteni" (Plant Protection Bulletin), a quarterly journal containing original articles by Turkish scientists and abstracts from foreign literature.

The technical competence of the staff is very high. Most of them are graduates of Ankara University, and some have considerable experience in their subject. Several have spent periods varying from some months to two years at academic or governmental institutions abroad. All are extremely enthusiastic and eager to learn.

The Institute possesses a number of modern analytical instruments, such as polarograph, pH meters, electrical titrometer, refractometer, photometers, melting point apparatus, electrolytic analyser etc., as well as a number of analytical balances of the most up-to-date type. An infra-red spectrophotometer and a U.V.+visible range spectrophotometer are on order. When they are delivered, the laboratory will probably be one of the best instrumented, for its size, in the world.

On the other hand, the situation with respect to other types of equipment was most depressing at the time of the expert's arrival. There was practically no glassware with intorchangeable ground-glass joints, and very few of the necessary reagents. Solvents, etc., were, and still are, intermittently in short supply. Heating apparatus and thermostatically controlled water baths are inadequate for the purposes envisaged. Even such equipment as test tubes, filter papers and glass tubing are chronically in short supply.

The biological laboratory lacks precision equipment for the production of repeatable insecticide appears. The present apparatus has been improvised lically and is giving comen tively good service, but will not, in the long run, satisfy requirements. An apparatus to deposit very small, accurately known, quantities of toxicants on individual insects probably will be needed. The expert is not qualified to comment on the equipment of the machinery section.

The greatest handicap for proper functioning is the present housing situation. When the Institute was founded in January 1958, a spacious building was planned in cooperation with foreign scientists, and a plot was acquired. Building operations were started during the summer of 1958, but they were suspended shortly afterwards and have not been recommenced at the time of writing. Efforts are now being made to resume work, but it will be at least the autumn of 1960 before the Institute can be properly rehoused. In the meantime, two suburban residential houses, totally unsuited as laboratories, serve as accommodation.

The worst sufferer from present conditions is the Chemistry section. There are no fume cupboards, and there is only one water tap, in their laboratories. Naked flames can hardly ever be used because the atmosphere is laden with solvents. The main bench is without services. Delicate microanalysis has to be carried out side-by-side with the testing of formulations containing a high proportion of insecticides, while immediately outside the laboratory dusting tests are performed. It is greatly to the credit of all concerned that they are doing so well under such appalling conditions.

SUMMARY OF ACCOMPLISHMENTS

It is clear that any benefits accrueing to the Turkish economy from the expert's stay must be long-term rather than immediate. Whatever was accomplished will manifest itself in the form of skills and facilities which will be more and more utilized as the Institute becomes fully functional. Furthermore, these skills are only a basis on which the staff concerned can, and must, improve as they gain experience with an ever-widening array of or bloms. Unavoluably, time and equipment were insufficient to train the workers in all aspects of residue analysis or cogent subjects they are likely to need. All that it is hoped was accomplished is a foundation of the correct outlook and the mode of working in a field new to the members of the Institute.

In accordance with his terms of reference, the expert laid much stress on the assay of posticide residues by chemical means. This obviously was the subject on which instruction was most needed. The analyses of formulations made by the Institute, both physical and chemical, were found to be good, and any improvements effected were matters of detail rather than principle. In the bio-assay section Dr. Hadaway had laid a sound foundation on which the workers themselves were able to advance. It was not possible to give any help to the machinery section, and assistance on the problem of inert materials was confined to establishing a contact abroad.

Immediately after his arrival in Turkey, it became evident to the expert that the Institute's resources in glassware and chemicals needed considerable augmentation if any kind of residue analysis was to be attempted. Considerable time was spent in compiling lists of the most urgent needs, and every effort was made to help the Institute to obtain these materials. The situation is now much improved. FAO has sanctioned the expenditure of about \$500 for standard ground-glass joint apparatus and reagents. Imperial Chemical Industries Limited has donated two Schechter-Hornstein apparatus for the micro-determination of BHC. and also some chemicals, including materials for chromatographic clean-up. E. Merck A.G., Germany, and Geigy S.A., Switzerland, have donated a wide array of chemicals. The Turkish Gov. rnment has now sanctioned expenditure for more glassware and chemicals to be bought abroad, and when these are delivered in a few months time, the Institute should be excellently equipped in these respects for all contingencies which can be foreseen at present. A few chemicals were obtained on the Turkish market or from university and similar institutions, and some pieces of glassware were made locally.

Determination of Physical Characteristics of Formulations

Internationally accepted methods in this sphere are not always infallible guides t field performance, particularly where dusts are concerned. The expert stressed the importance of carrying out all tests under strictly standardized conditions, and he recommended that WHO methods be used in all cases. In particular, it is necessary to carry out

suspensibility and emulsion stability tests under constant conditions, and to perform chemical analysis on the settled portion of suspensions. For the flowability of dusts there are no really good methods, but the one developed by the Shell Company is probably the best. In its performance particular care must be taken to avoid electrostatic effects.

In the absence of guidance in the agricultural field under local conditions, the Institute uses WHO specifications as criteria for the acceptance of formulations. This is the best course until more is known about the characteristics required for the types of applications actually intended.

Determination of Chemical Properties of Formulations

The analysis of the BHC and DDT content of formulations, either in the presence of each other or separately, was found to be satisfactory, but eletrimetric titration was taught in order to speed up the final assay of chlorine. Attempts to obtain reliably reproducible results in the assay of the gamma isomer of BHC with the polarograph were unsuccessful, probably due to the interference of stray currents from other apparatus and the laboratory wiring system. Chromatographic separation, as previously practised, is still the best method available. This method can also be used to estimate the aldrin content of formulations. For other chlorinated hydrocarbons, the total chlorine method according to Stepanov, as already known to the staff, will serve for most purposes. The estimation of total chlorine by combustion has also been successfully demonstrated but, for safety reasons, can only be carried out in the present premises when the atmosphere is free of selvent vapours. The Phenyl-azide method for Diels-Alder condensates is impracticable and unsafe under present conditions.

For the analysis of phosphoric esters, only the total phosphorous method was available. This is still best for a number of such compounds, but for parathion and malathion speedior and more specific methods, based on WHO procedure, were introduced.

Chemical Residue Analysis

All chemical assay of small amounts of pesticides in plant or animal material depends on successful clean-up of interforing substances. Every crop and every chemical poses its own problem, and literature is not always an infallible guide. It was found, for instance, that DDT on alfalfa could not be cleaned up satisfactorily by a sulphuric acid column, as often recommended, and an additional step involving the use of an activated alumina column was necessary. Among the clean-up methods now available to the Institute, which have been demonstrated with one or the other method, are:

(1) passing through a column containing fuming sulphuric acid on diatomaceous earth; (2) passing through a column of activated alumina; (3) passing through a column of activated charcoal; (4) paper chromatography for chlorinated hydrocarbons and for phisphoric esters; and (5) removal of glycerides by saponification with alcoholic potash.

Instructions on clean-up by partitioning between immiscible solvents were given in writing but could not be demonstrated as the necessary materials were not available in time. It will be necessary for the staff to establish, by careful experimentation for each problem, what procedure is best.

For the assay of chlorinated hydrocarbons, three methods were taught:
(1) the Micro-Stepanov method, applicable to all chlorinated hydrocarbons;
(2) the Schechter-Haller method, specific to DDT; and (3) the SchechterHornstein method, specific to BHC. By judicious use of the three methods,
all residue problems at present foreseen with these compounds should be
capable of solution. The Micro-Stepanov method has proved very suitable
for the assay of hexachlorobenzene on grain, a fact which is mentioned here
as it does not appear to be previously recorded and as it is so important
in Turkey. The Schechter-Haller method requires the most meticulous cleanup, but is otherwise the easiest and quickest.

For phosphoric esters in general, two methods are available. One is an estimation of total phosphorus (as has been previously practised in the laboratory for formulations) after suitable clean-up procedures, e.g., activated alumina and charcoal columns followed by extraction with petroleum ether. This method has the disadvantage that some harmless metabolites of the pesticide may also be estimated. For most purposes, a better procedure is the assay of the anti-cholinesterase activity of the residue. For this human plasma is usually recommended, but, being unable to separate the erythrocytes efficiently from blood obtained from the blood bank, whole human blood was used with satisfactory results. The method is applicable to all phosphorics which are either in vitro cholinesterase inhibitors or can be converted into such by oxidation in a benzene-acetic acid-hydrogen peroxide system. The method was taught with parathion. In connection with paper chromatography it should be possible to estimate some compounds in the presence of each other.

The cholinesterase inhibition method was successfully used for the estimation of diazinon in olive oil and in clives. A clean-up procedure involving the extraction of the oil with methyl alcohol, and of the methyl alcohol with water prior to exidation, has been worked out. This method, by which quantities from 1 - 5 microgrammes of diazinon can be estimated, has not been described in the literature, and it is hoped to publish it in due course.

Malathion on hazel-nuts was estimated by an adaptation of the WHO method for formulation analysis.

Parathion and other phosphoric esters with a p-nitrophenol group can be estimated also by a simple and quick colorimetric reaction with N(1-naphthyl) ethylene diamine.

For the detection of mercury residues on grain a quick and simple qualitative technique with aluminium foil and alkali was taught. Quantitatively, mercury on grain was measured in quantities from 1 - 5 microgrammes by the dithizone method for which the apparatus was produced locally. This method is also applicable to mercury residues on fruit.

Sulphur residues were estimated by digestion of the plant material with hydrobromic acid and subsequent formation of methylene blue in a special apparatus, also made locally. This method can be used for the estimation of deposits of wettable sulphur and lime sulphur, and also for sulphur-containing chemicals such as Captan.

Captan residues can also be determined by two other colorimetric methods. One of these, very quick but not very accurate or pleasant to perform, involves a reaction with tetraethyl ammonium hydroxide in pyridine,—the other one, more lenghthy but also more accurate, a reaction with resorcinol. The latter depends on the correct grade of charcoal for clean-up being available.

Biological Residue Analysis

On arrival in Turkey it was found that the members of the bio-assay sections already possessed a sound knowledge of the principles of estimating pesticides by biological means, including the statistical assessment of their results. The film technique was chiefly employed, using the beetles Tribolium castaneum and Sitophilus granaria, and a wingless mutant of Drosophila. The laboratory was unfortunate in losing its cultures of Drosophila as the benzoic esters used to protect the medium against fungi were no longer available. New supplies have now been secured and the culture has been restocked from Switzerland.

The use of the film technique for residue analysis was successfully demonstrated by assaying the dieldrin deposits from a thermal fog in a locust trial. Exposed surfaces were washed with acetone and the dieldrin content of the solution estimated on evaporated deposits with Tribolium and Sitophilus.

The most important help given to the section consisted of the introduction of a culture of the mosquito Aedes acgypti which is now successfully being bred after some initial difficulties. The aquatic larvae, particularly the earlier stages, are so sensitive that satisfactory ranges of kill can be obtained within the water solubility of all contact insecticides in use in the country. They can be bred easily in large quantities, and the use of test insects in a true solution eliminates errors due to fumigant action or differences in motility. It should be possible to use this technique with accurate results, provided controls with known amounts of the poison under test are included in each experiment. The only group of insecticides known to the expert to which it is not applicable are the systemics, which are not at present used in Turkey.

Future Work

It is desirable that the staff of the Institute should have an opportunity to practice the new methods acquired on a practical research program extending over several seasons. Such a program can also provide much needed information on which the Gevernment can base regulations with regard to

tolerances of pesticides. It is suggested that experiments should be undertaken in cooperation with the Istanbul Plant Protection Institute, in which the fate of the spray deposits obtained by the normal procedure on cherry and on olive is followed from application to harvest. Both chemical and biological assay methods are to be used. In the first year, this experiment should be kept as simple as possible, but in subsequent seasons a limited number of different treatments, varying in the dates and numbers of application, might be compared.

CONCLUSIONS AND RECOMMENDATIONS

General Assessment and Further Training

The chemical control of formulations carried out by the Institute can be regarded as entirely satisfactory. The staff is perfectly capable of carrying out analysis of all the posticides at present on the Turkish market with sufficient speed and accuracy. There is ample literature on the subject and, when new pesticides are introduced for registration or sale, the manufacturers usually supply details of reliable methods for chemical estimation. There is no reason to suppose that with the equipment available, or shortly to be made available, all such methods can not be mastered.

The same applies to the assessment of the physical properties of formulations. The skills and the equipment are available and are being used competently. A proviso must, however, be made in this connection concerning the inadequacy of published methods. For instance, there are no really satisfactory laboratory tests for the field performance of dust formulations, particularly flowability. There is very little guidance which will ensure that specifications laid down will actually produce a formulation suitable for the purpose and the mode of application envisaged. The Institute works according to THO specifications wherever possible, and this is probably the best course. It must, however, be remembered that these specifications were not drawn up for agricultural purposes and cannot be regarded as an infallible guide in every instance.

Much more training and experience will be needed to make residue analysis, both chemical and biological, fully functional for the high standard and the multitude of purposes required. Most of this training will be acquired by the experience the staff is progressively expected to gain on the basis now provided, but further training abroad is also being provided. Mr. Talip Oden is at present working on general bio-assay techniques at Rothamsted Experimental Station, England, on an FAO fellowship, and Mrs. Cânâ Otaci will go to the Flant Pathology Laboratory, Harpenden, England for 9-12 menths under the suspices of CENTO to be trained in microchemical analysis.

The testing of machinery for application of pesticides is a definite weakness. The staff, though capable and enthusiastic, lacks guidance on methods. The services of an expert from abroad to work at the Institute on this problem would be of great benefit.

Another weakness is found in the search for suitable native inert materials for incorporation in home-produced posticide formulations. This is an important aspect of the Lastitute's work. It can confer great benefits on the economy by the saving of foreign currency and can help in the establishment of an efficient Turkish industry. Adequate facilities for such research do not exist within the industry itself. This search requires special techniques and apparatus, and it is suggested that the best way to deal with the

matter would be through a period of study abroad for a member of the Institute. Accordingly it is recommended that a member of the staff be awarded a fellowship tenable for about six months. He or she should preferably work in an industrial laboratory.

Equipment

The greatest handicap of the Institute at present is the inadequacy of its premises. The lack of fume cupboards, adequate water and gas supply and the impossibility of functional separation of the work into distinctly accommodated units makes for waste of time and material, and, in some cases, even danger to personnel. Accurate residue analysis can not be carried out in an atmosphere of solvent vapour or in rooms likely to be contaminated with the materials under test. It should be performed in separate rooms and with glassware not used for any other purposes. Similarly, in the present constant temperature rooms it is not possible to produce really standardized material for bio-assay, and this again adds to the work by increasing the number of control experiments to be carried out with each bio-assay test. It is urged that every effort be made to press ahead as speedily as possible with the new building construction, which has been held up so long, so that the Institute can become fully functional.

During the expert's stay in Turkey, shortage or absence of chemicals and glassware posed considerable problems. When all the equipment now on order, or proposed to be ordered, has been delivered, the Institute can be described as well-equipped with instruments, glassware and reagents. It will, however, still need a constant supply of many necessities, such as solvents, etc., and minor items of capital equipment. None of these may be costly in themselves, but shortages, however temporary, will inevitably entail the waste of very expensive manpower and time.

The present system of making single, and comparatively large, foreign currency allocations only occasionally has certain disadvantages. Future needs cannot possibly be accurately foreseen, and supplies are ordered on the basis of present needs only. In consequence, if problems and methods should change, as they are bound to do from time to time, there may be insufficient supplies of certain commodities while others in stock are not used. It would be more economical to allot a sum each year to be spent as and when required.

Organization

When the Institute has been adequately rehoused, and space and equipment will allow for functional separation of the various types of work, it would be of advantage to reallocate sections as follows:

- (1) A pesticide formulation control section, testing physical and chemical properties of all formulations submitted.
- (2) A residue assay section, with biological and chemical sub-sections or, alternatively, two independent sections.

(3) A machinery section, as at present.

To these might be added later a toxicological section. The sections would, of course, continue to share certain apparatus and services. Some problems might be divided between two sections, e.g., the inert materials research between the formulation and machinery sections.

The publication of "Bitki Koruma Bülteni" could be combined with the library service into a small independent section.

The work of the Institute is likely to grow considerably over the next few years, particularly through residue problems. On the other hand, it could be considerably lightened by placing the responsibility for the routine examination of production batches on the formulation industry. The Institute should retain over-all control by laying down specifications, by designating methods of analysis to be followed in the industrial laboratories, by periodic inspection of, and consultation with, the laboratories and by occasionally checking. Home-produced formulations would then be on the same footing with regard to registration and control as imported ones.

It is urgently recommended that plans for a laboratory capable of dealing with problems of the toxicology of pesticides be given earnest consideration. Without such a unit, the skills acquired in residue determination will not be used to the fullest extent. This unit need not necessarily be attached to the Institute, but should in any case collaborate closely with it. A brief visit to some government toxicological laboratories abroad, by someone concerned with drawing up the terms of reference and deciding on size and equipment, might be advisable.

Cooperation With Other Government Bodies

A serious weakness at present is the lack of data on which to base specifications for pesticide formulations. This could be improved by close cooperation between the Institute and the six Plant Protection Institutes in a research program to provide these data. At present too much reliance is placed on information obtained from abroad. Only trials carried out against indigenous pests with the machinery available locally can give a sound basis for the physical and chemical properties to be demanded of approved formulations.

It is understood that no service similar to the one given by the Institute is at present available for pesticides used other than in crop production, e.g., veterinary purposes, public health and the protection of stored products. In order to avoid needless duplication of manpower and equipment, it is recommended that the Ministry of Agriculture offer the services of the Institute to the other Government departments concerned. In such manner the best use may be made of the specialized skills and apparatus in the interest of the Turkish economy as a whole. Until the Institute is well-established in its new premises, however, it can not undertake more than a moderate amount of additional duties.

